

# DIRECT DETERMINATION OF PALLADIUM WITH FURILACROLEINEOXIME BY ULTRAVIOLET SPECTROPHOTOMETRY

José Antonio SILVA COELLO\*  
Ronélio RODRIGUEZ-HERNANDEZ\*

■ **ABSTRACT:** A simple extraction spectrophotometric method for the determination of palladium traces in a mineral sample is described. The suggested method is based on the liquid-liquid extraction of complex palladium with furilacroleineoxime into chloroform. The best experimental conditions are pH range 3.0-9.0 and ratio 20:1 (FAO/Pd concentration). Beer's Law is obeyed for 0.1-1.0 mg/L of palladium. The developed procedure has been applied successfully to the analysis of palladium traces in mineral samples without any separation.

■ **KEYWORDS:** Colorimetric determination; liquid-liquid extraction; furilacroleineoxime; palladium.

## Introduction

Organic reagents have been widely used in Analytical Chemistry for spectrophotometric determination of various metals, providing methods with good selectivity and sensitivity.<sup>3,5-6</sup>

Nevertheless, few determination methods are proposed in the literature<sup>1,8-9</sup> for determination of palladium in the presence of high concentration of other transition elements, as required usually in mineral analysis.

A spectrophotometric method for the determination of Pd(II) with furilacroleineoxime (FAO) has been reported.<sup>7</sup> This method is efficient but it has not yet high selectivity, due to interferent effects of other species that might be present in the matrix. The purpose of the present work was to use extraction spectrophotometric technique for the determination of palladium with furilacroleineoxime in mineral samples. In addition, it was established the optimum conditions for FAO-Pd complex formation, its stoichiometry and interference effects.

\* Faculty of Chemical Engineering and Pharmacy - University of Camaguey - Camaguey - Cuba.

## Materials and methods

### a) Apparatus and reagents

A CF-26 uv-visible spectrophotometer with 1.0 cm pathlength quartz cells was used. Measurements of pH were carried out with a METROHM pHmeter using a combined glass-calomel electrode.

All reagents were of analytical-reagent grade.

Stock solution of palladium (II) chloride  $2.5 \times 10^{-4}$  mol/l was prepared and standardized gravimetrically.

FAO solution  $10^{-3}$  mol/l was prepared by dissolving the pure compound (synthesized in our laboratory from furfural) in ethanol (20% v/v).

Acetate buffer solutions were prepared from acetic acid-sodium acetate.

### b) Procedure of extraction method

Transfer a suitable aliquot of sample solution containing up to  $10^{-6}$ - $10^{-5}$  mol/l of palladium into a 50 ml beaker. Add with mixing 1.5 ml of FAO  $10^{-3}$  mol/l and buffer acetate. Adjust the pH to 5.0 using a pHmeter. Pipette 5 ml of chloroform into the beaker and shake for one minute. After 10 minutes the chloroform layer is transferred into a volumetric flask. The absorbance of that phase is measured at 360 nm, in the presence of a blank obtained in an identical way.

## Results and discussion

The absorption spectra of the complexes FAO-Pd obtained in hydroalcoholic medium ( $10^{-3}$  mol/l) show an absorption maximum at 333 nm. On the other hand the same complex extracted in chloroform at pH 5.0 and concentration ratio of 20:1 for FAO:Pd gives a spectrum that exhibits an absorption maximum at 360 nm ( $\epsilon = 8.5 \times 10^4$  l. mol $^{-1}$ . cm $^{-1}$ ). From this comparison it should be clear that it is possible to analyse the complex in chloroform phase.

### a) Selection of optimum reaction conditions

The effect of the shaking time, pH and optimum relation [FAO]/[Pd] were investigated. The results show that the extraction method exhibit a yielding of 98%

after one minute of shaking time and the signal of the complex is very stable in chloroform phase.

The optimal pH for the liquid-liquid extraction and subsequent determination was studied by adjusting the pH in the pH range 1.8 - 9.4. The results obtained are shown in Figure 1. From this Figure, it is possible to conclude that the optimal pH for formation and subsequent extraction of the complex FAO/Pd is 3.0 - 9.0. Hence pH = 5.0 was chosen for further studies.

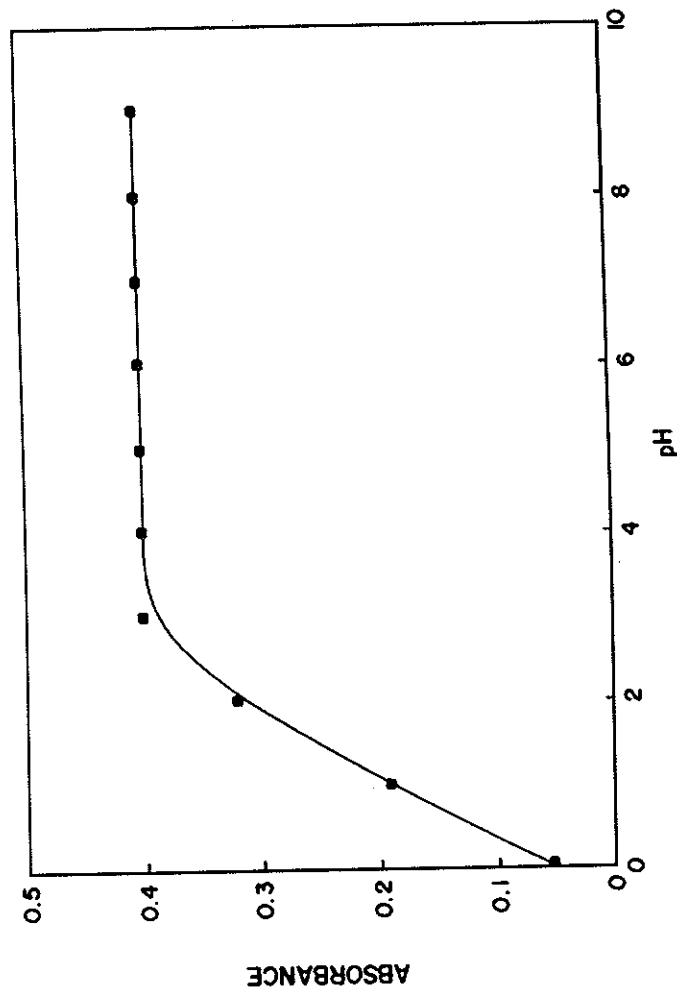


FIGURE 1 - Effect of pH on complex formation.

The results obtained on the investigation of the effect of FAO concentration for the formation and extraction of the FAO-Pd complex are shown in Figure 2. It is clear that a minimum of 20:1 (concentration ratio of FAO/Pd respectively) are enough for maximum absorption, which signal is stable. A stoichiometry 2:1 of the complex FAO:Pd was determined previously<sup>2,4</sup> and the stability constant was  $3.5 \times 10^{16}$ .

Table 1 - Maximum values of concentration of strange ions that do not interfere in the determination of 0.1 mg/L of palladium with FAO

Strange ions	Tolerance (mg/L)
Cu(II), Ni(II), Mo(IV) and Ti(III)	50,0
Fe(III) and Pt(II)	12,5
Mg(II), Al(III), Cr(III), Co(II), Cl <sup>-</sup> , Br <sup>-</sup> , citrates and tartrates	100,0
PO <sub>4</sub> <sup>3-</sup> , oxalate and F <sup>-</sup>	100,0
I <sup>-</sup> and SCN <sup>-</sup>	5,0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	1,0

#### d) Analysis of real samples

The proposed method was applied in the analysis of palladium in a mineral sample of nickel (II) and copper (II) sulphide. The results obtained were compared with those obtained by gravimetry. A good agreement between the two methods was obtained, with the values of  $2.34 \pm 0.07$  for the proposed method and  $2.39 \pm 0.02$  for gravimetric method.

#### Conclusions

This work demonstrates that the proposed extraction spectrophotometry method is a simple, selective and useful method for the determination of palladium in mineral samples using furilactroleineoxime.

SILVA COELLO, J. A., RODRIGUEZ-HERNANDEZ, R. Determinação direta de paládio com furilactroleineoxima por espectrofotometria de ultravioleta. *Ecl. Quím. (São Paulo)*, v.20, p.89-94, 1995.

- RESUMO: Um método espectrofotométrico para determinação de paládio usando furilactroleineoxima em meio de clorofórmio é descrito. A lei de Beer é obedecida no intervalo de 0,1-1,0 mg/L de paládio. As melhores condições de análise são pH 3,0-9,0 e razão molar 20:1 ligante/paládio. O método desenvolvido permite a determinação direta de traços de paládio em amostras de mineral.
- PALAVRAS-CHAVE: Determinação espectrofotométrica; furilactroleineoxima; paládio.

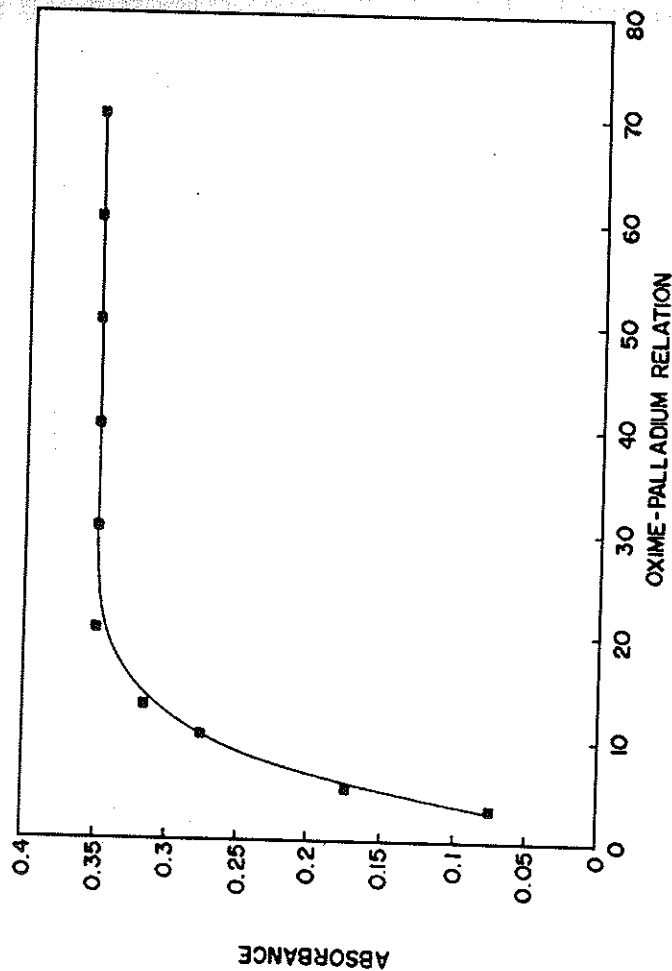


FIGURE 2 - Saturation curve.

#### b) Calibration graph

Under the optimal instrumental parameters and reaction conditions established above, a linear calibration graph was obtained by plotting the absorbance measured at FAO-Pd complex spectrum for palladium in the concentrations range 0.1-1 mg/L, following the equation:  $y = -5.71 \cdot 10^{-3} + 86.825 \cdot 4 x$  (correlation coefficient = 0.999).

#### c) Interference studies

The interfering effects of various foreign ions on the determination of 0.1 mg/L of palladium is summarized on Table 1. Analysing the tolerance limit it is possible to conclude that no interference is significant for determination of palladium between 0.1-1 mg/L even in the presence of higher concentrations of several cations and anions.

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